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(71) Applicant: Kamyr, Inc.  
Ridge Center  
Glens Falls New York 12801-3686(US)

(72) Inventor: Greenwood, Brian F., c/o Kamyr, Inc.  
Ridge Center  
Glens Falls, New York, 12801-3686(US)  
Inventor: Funk, Erwin D., c/o Kamyr, Inc.  
Ridge Center  
Glens Falls, New York, 12801-3686(US)  
Inventor: Jlang, Jian, c/o Kamyr, Inc.  
Ridge Center  
Glens Falls, New York, 12801-3686(US)  
Inventor: Delcourt, Thomas R., c/o Kamyr, Inc.  
Ridge Center  
Glens Falls, New York, 12801-3686(US)  
Inventor: Phillips, Joseph R., c/o Kamyr, Inc.  
Ridge Center  
Glens Falls, New York, 12801-3686(US)

(74) Representative: UEXKÜLL & STOLBERG  
Patentanwälte  
Beselerstrasse 4  
W-2000 Hamburg 52(DE)

(54) Tumbling ozone reactor for paper pulp.

(57) A method of delignifying comminuted cellulosic fibrous material (paper pulp) at a consistency of about 30-45% employing ozone as the active bleaching component, and capable of utilizing a variety of different reactor designs. In each case the paper pulp is fluffed (with 18) and ozone gas is added to it (at 22, 24), and the pulp is maintained in contact with the ozone containing gas while it is tumbled to keep it loose, and homogenous, with a high surface area to volume ratio. The reactor (23, 223) may be just below a fluffer (18), and may include a short screw section (247) only adjacent the pulp inlet (22, 222) and radially extending paddles

(64) provided along the rest of the length of the shaft (248). The paddle distal tips (67) have a tangential velocity sufficient to impart a ballistic velocity to the pulp such that the arc described by the particles follows the arc of the vessel shell. Alternatively, tumbling may be provided by rotating a tubular reactor shell (71) about an axis which slants downwardly with respect to the horizontal. Lifters (80) may be provided extending inwardly from the inner circumferential periphery of the rotating shell. The lifters usually being provided just at the discharge end (78) of the shell to lift the treated fluffed pulp into a discharge mechanism (81).

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## BACKGROUND AND SUMMARY OF THE INVENTION

It has been known for more than one hundred years that ozone is an effective material for delignifying comminuted cellulosic fibrous material (paper pulp). There have been literally dozens of proposals of mechanisms for implementing this general knowledge, but at the present time there are no known commercially viable systems. One reason for this is that the ozone delignification reaction is much quicker than the reaction with most other bleaching chemicals. Exposure of cellulosic material to ozone containing gas for 15 seconds or less typically is sufficient to effect delignification of the material actually exposed. This is combined with the fact that it is very difficult to obtain a high concentration of the active ingredient -- ozone -- in ozone bleaching systems since the maximum concentration of ozone possible in air under present technology is about two to three percent, and with essentially pure oxygen gas as the carrier the theoretical present technology limit is only about 11 to 12%, while the practical limit is about 4 to 8%.

Because of the high reactivity rate of ozone, it is necessary that pulp not be exposed too long to effective amounts of ozone since the ozone may attack the cellulose and thereby weaken the pulp substantially, rather than just delignifying it, regardless of the presence of viscosity protectors. It is very difficult to maintain the pulp -- especially at the 30-45% consistency range for which treatment is most practical -- so that it is loose and has a high surface area to volume ratio. There is a great tendency for the pulp to form into nodules or clumps, which causes over exposure of the surface pulp to the ozone, possibly resulting in severe degradation of the cellulose of the surface pulp, while the pulp in the interior of the nodules or clumps is not treated at all.

According to the present invention, a method and apparatus are provided which maintain the pulp and ozone gas in appropriate relationship so that the pulp may properly react with the ozone gas, yet will not be over exposed thereto. A number of different reactor designs are within the scope of the invention, and can accomplish such desirable results. The basic feature in common to all of the reactor designs -- and a basic part of the practice of the method steps according to the invention -- is the effective tumbling of the pulp while it is maintained in contact with the ozone containing gas, to keep the fluffed pulp loose and homogenous, with a high surface area to volume ratio. Also, a significant aspect of the present invention is the introduction of ozone containing gas into the reactor at a plurality of different points along the

path of movement of the pulp within the reactor, with withdrawal and recycling of the gas. Such a cross flow of gas to the tumbling pulp provides a very effective interrelationship for reaction. Also the fact that the gas is introduced, withdrawn, and recycled, makes maximum utilization of the ozone within the gas, and thereby minimizes the volume of bleaching fluid (due to the low concentration of ozone possible).

According to one aspect of the present invention, a method of delignifying acidified comminuted cellulosic fibrous material at high consistency is provided. The method comprises the steps of: (a) Fluffing the material so that it is loose, with a high surface area to volume ratio. (b) Adding ozone containing gas to the material, the amount of ozone added being effective to delignify the material. And, (c) maintaining the material in contact with ozone containing gas for at least a few seconds, while tumbling the material to keep the fluffed material loose and homogenous, with a high surface to volume ratio, well mixed with the ozone containing gas. Step (c) is preferably practiced by simultaneously tumbling the material and conveying it in a first direction. There also preferably is the further step (d) of continuously introducing ozone containing gas flowing in a second direction generally perpendicular to the first direction into contact with the material during the practice of step (c), such as by -- at various places along the path of the material as it moves in the first direction -- continuously introducing and withdrawing ozone containing gas from contact with the material by introducing it someplaces along the path gas withdrawn from a previous place along the path.

A number of different reactor designs are provided according to the invention for use in apparatus for delignifying paper pulp using ozone containing gas. The apparatus includes a fluffer for fluffing the paper pulp so that it is loose and has a high surface area to volume ratio, and a tubular shell defining the ozone reactor. A pulp inlet to the tubular shell is provided adjacent a first end thereof and a pulp outlet adjacent a second end thereof. A conveyance means conveys the pulp from the inlet to the outlet, and means are provided for effecting tumbling of the pulp as it moves in the reactor from the inlet to the outlet so that the pulp remains loose with a high surface to volume ratio. The reactor designs differ in the conveyance and tumbling mechanisms.

According to a preferred design according to the invention, the reactor includes a short screw section at the pulp inlet for effecting conveyance, and a plurality of paddles extending from the shaft of the screw section, along the length of the reactor. The paddles may have angled faces, which also assist in conveyance. The paddles act as

lifters to lift the pulp and properly expose it to the ozone containing gas. Gas is preferably introduced at a plurality of points along the shell, at the bottom, and withdrawn from the top, and a vent is provided at the end of the path of movement.

According to another design of reactor according to the invention, the shell is disposed so that its central axis slopes downwardly from the inlet to the outlet, which effects the conveyance. The shell is rotated about its axis at a speed which is sufficient to move the pulp to the top of the shell so that it falls downwardly therefrom, but insufficient to cause the pulp to continue along with the shell as it rotates. Lifters extending inwardly from the inner circumferential surface of the shell at the pulp outlet may be provided for lifting, to put it into a discharge structure at the outlet of the shell.

Other reactor designs according to the invention include screws with flights extending substantially the entire length of the interior of the reactor shell, with either paddles extending outwardly from the screw shaft and interspersed with the flights, or lifters extending axially from peripheral portions of the screw flights. The paddles and lifters may be disposed at the same or different angles, single or multiple screws may be provided (e.g. two counter rotating screws within the same reactor shell to improve the mixing action of the pulp with gas during conveyance), and differing mechanisms for introducing and/or recirculating the ozone containing gas during conveyance.

It is the primary object of the present invention to provide for effective contact of comminuted cellulosic fibrous material with ozone containing gas by tumbling the material to keep it fluffed and loose and homogenous, with a high surface area to volume ratio, during ozone bleaching of the material. This and other objects of the invention will become clear from an inspection of the detailed description of the invention, and from the appended claims.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

FIGURE 1 is a schematic of an exemplary apparatus for effecting ozone bleaching according to the invention;

FIGURE 2 is a schematic of a second exemplary embodiment of apparatus according to the invention, utilizing a pneumatic feed system;

FIGURE 3 is a side view, partly in cross-section and partly in elevation, of a first embodiment of an exemplary ozone reactor according to the invention;

FIGURE 4 is a perspective view of the screw of the reactor of FIGURE 3;

FIGURE 5 is a perspective view of an alternative embodiment of screw which may be utilized with

the reactor of FIGURE 3;

FIGURE 6 is a side schematic view, partly in cross-section and partly elevation, of a second exemplary embodiment of reactor according to the invention;

FIGURE 7 is a top view, partly in cross-section and partly in elevation, of a third embodiment of reactor according to the invention;

FIGURE 8 is a view like that of FIGURE 3 for a fourth, preferred, exemplary embodiment of a reactor according to the invention;

FIGURE 9 is a longitudinal sectional view of the shaft, with paddles, of the reactor of FIGURE 8, taken along lines 9-9 thereof;

FIGURE 10 is a side schematic view, partly in cross-section and partly in elevation, of a fifth embodiment of reactor according to the invention; and

FIGURE 11 is an end cross-sectional view - taken along lines 11-11 of FIGURE 10 -- of the reactor of FIGURE 10..

#### **DETAILED DESCRIPTION OF THE DRAWINGS**

An exemplary apparatus according to the invention, for practicing a method of delignifying comminuted cellulosic fibrous material at high consistency, is illustrated in FIGURE 1. Comminuted cellulosic fibrous material (paper pulp) is fed in line 10 to a first mixing tank 11 wherein it is mixed with a protector from source 12 -- such as  $MgSO_4$  -- and acid from source 13 -- for example  $H_2SO_4$  --, and is diluted with water or recycled filtrate to a consistency appropriate for feed to the particular thickening device chosen (generally 1-10% BD for typical thickeners) and then is pumped via pump 14 to a conventional thickener 15, such as a press. Additional acid from source 13 may be added at the press 15, so that the pulp has a pH of about 1.5-4.0, typically about 1.8-3.5, and preferably about 2.5-3.0. The pulp is thickened so that in discharge line 16 it has a high consistency, typically over 20% and preferably about 30-45%. It is fed to conventional shredder 17 where large chunks of pulp are broken up into smaller chunks and then to conventional fluffer 18 where the pulp is acted upon so that it becomes very loose, with a high surface area to volume ratio, and no large pieces. Preferably, some ozone containing gas from ozone generator 19 is added via line 20 to the fluffer 18. The ozone is made by the conventional ozone generator from oxygen from source 21, and it is desirable to obtain as high a concentration of ozone in the discharge line 20 as possible, which under present technology is about 4 to 8%, although theoretically it could be as high as 11 to 12%. It is preferred that the ozone be in oxygen as the carrying gas since the highest concentration of

ozone practical in other carrying gases, such as air, is about two to three percent. Of course there may be other gases in the carrying gas in line 20 as long as they do not adversely impact upon the bleaching action of the ozone, in fact other common bleaching fluids (e.g. liquids) may also be added thereto, such as hydrogen peroxide.

From the fluffer 18, the pulp is fed directly into pulp inlet 22 for the ozone reactor 23. Ozone is preferably added to the reactor 23 in line 24 which branches off of line 20 from generator 19. Typically the reactor 23 is generally horizontal, while the ozone flows generally vertically from the bottom of the reactor, cross-current to the flow of pulp within the reactor 23 from the pulp inlet 22 to the pulp outlet 25. Preferably, recycle of the ozone gas is provided utilizing fans 26 and inlets 27, ozone gas at the top of the reactor 23 being withdrawn by a fan 26 and fed back into the bottom of the reactor, downstream, utilizing inlets 27. The residual ozone in these recycle lines may be sensed using sensors 28, and the flow rate in the line 24 modified by flow controller 29 in response to this sensing. Above the pulp discharge 25, a gas vent 30 preferably is provided.

From the reactor 23, the bleached pulp is discharged in discharge conduit 25 directly into the top of a second mixing tank 31, in which tank the consistency is lowered by adding liquid from filtrate source 32. A medium consistency pulp ensues, which may be pumped by the medium consistency pump 33 for subsequent processing. Likewise, the pulp may be diluted further in order to feed a low consistency inlet washer.

While the temperature and pressure of the delignification reaction is not particularly critical, it is preferred that the temperature be maintained within the general range of about 20-50°C within the reactor 23, and that the pressure be maintained within the range of slightly sub-atmospheric to about 15 psi. By proper control of the venting from vent 30, and flows of ozone containing gas from source 19, a slightly sub-atmospheric pressure may be maintained. A slightly sub-atmospheric pressure can be desirable since ozone gas leaking from the reactor 23 (if any) could cause a safety problem, and if the reactor 23 is slightly sub-atmospheric, ozone gas will not leak therefrom.

FIGURE 2 illustrates another exemplary apparatus according to the present invention, similar to that in FIGURE 1 except that the pulp is pneumatically conveyed from the fluffer to the reactor. In FIGURE 2, identical components to those in the FIGURE 1 embodiment are shown by the same reference numeral while modified components are shown with the same reference numeral followed by a "'".

In the FIGURE 2, embodiment, the pulp from

press 15 is fed to shredder 17 and fluffer 18. At the discharge from the fluffer 18, the pulp is entrained in a flow of gas from blower 34. The gas from blower 34 is preferably primarily oxygen, with a maximum concentration of ozone (e.g. about 4-8% using current ozone generation technology). The pulp is intimately mixed with the ozone containing gas as it is conveyed in discharge line 35 from blower 34, and the delignification reaction starts to take place. At the top of the ozone reactor 23', a gas/solids separator -- such as a conventional cyclone 36 -- is provided to separate the vast majority of the ozone containing gas from the pulp prior to feed of the pulp into the inlet 22' to the reactor 23'. The separated ozone containing gas is conveyed in line 37 back to the line 20', and subsequently to the blower 34.

After treatment in the reactor 23', the pulp discharged in discharge line 25' passes to conventional repulper 38, and then to standpipe 39 where it is returned from high consistency back to low or medium consistency, and it is pumped by low or medium consistency pump 40 for further processing.

The retention time in the reactor 23, 23' will vary depending upon the volume of pulp therein, the concentration of ozone gas achievable by the ozone generator 19, and the consistency of the pulp. Typically, however, the time in the reactor is at least a few seconds, and for an exemplary reactor 23, 23' having a length of 28 feet and a diameter of 7 feet, the retention time would be about one minute, and for a reactor 23, 23' having a length of 40 feet and a diameter of 10 feet the retention time would be about three minutes.

FIGURE 3 illustrates the details of an exemplary reactor 23 which could be used in either the FIGURE 1 or 2 embodiments.

The reactor 23 in FIGURE 3 includes a tubular reactor shell 41 to which the pulp, with some oxygen and ozone, is introduced in inlet 22, and from which it is withdrawn in outlet 25. Mounted concentrically within the tubular shell 41 is a shaft 42, which is preferably powered by a conventional motor 43. Bearings 44 for mounting the shaft 42 are provided at the opposite ends of the shell 41. Disposed on the shaft 42 within the shell 41 is a means for conveying the pulp from the inlet 22 to the outlet 25 in direction 45, as well as means for effecting tumbling of the pulp as it moves in the reactor, so that the fluffed pulp remains loose with a high surface to volume ratio so that the reaction with the ozone containing gas will be as uniform and quick as possible.

In the embodiment illustrated in FIGURE 3, the conveying means comprises a screw 46 having a plurality of screw flights 47; as the shaft 42 is rotated by the motor 43 the screw flights 47 con-



vey the pulp in the direction 45. Means for effecting tumbling of the pulp as it is conveyed comprises lifters 40. As is clear from both FIGURES 3 and 4, the lifters 40 preferably comprise plates which extend outwardly from the surfaces of the flights 47. Preferably the lifters 40 are disposed every approximately 90° along each face of each flight 47, adjacent to the circumferential periphery 49 of each flight 47. The lifters 40 serve -- upon rotation of the shaft 42 -- to engage the fluffed pulp, lift it up above the normal level of pulp within the reactor shell 41 so that it is uniformly exposed to the ozone containing gas flowing cross-currently within the shell 41, and then allow it to drop back down toward the bottom of the shell 41. Support legs 52 (with or without springs) -- similar to those in conventional steaming vessels -- support shell 41.

As can be seen from FIGURE 3, any number of fans 26 and recycle inlets 27 may be provided for effecting recycle of the ozone containing gas. Optimally, the gas discharged in vent 30 has little remaining ozone, most of the ozone having reacted during movement of the pulp in direction 45 within reactor 23. In this way, the volume of gas that need be handled is minimized, making utilization of the reactor 23 economically attractive.

FIGURE 5 shows another embodiment of screw, the corresponding components in this embodiment being shown by the same reference numerals as in the FIGURES 3 and 4 embodiment only followed by a "'". In this embodiment, instead of the screw flights 47' being continuous, they are interrupted at several portions along the length of the screw 46', as indicated by the gaps 50 in FIGURE 5. If desired, within the shell 41 a baffle plate 51' (see in dotted line in FIGURE 5) may be provided at each gap 50, to prevent ozone containing gas from flowing along the top of the reactor directly to the vent 30, rather ensuring passage of ozone containing gas within the recycle pathways defined by the fans 26 and inlets 27.

FIGURE 6 illustrates another embodiment of an exemplary ozone reactor according to the present invention. In this embodiment structures comparable to those in the FIGURE 3 embodiment are illustrated by the same reference numeral only preceded by a "1".

The reactor 123 has the same basic pulp conveying structure as the FIGURE 3 embodiment, namely a screw 146 having flights 147. However the means for effecting tumbling of the pulp in the FIGURE 6 embodiment is different. The tumbling means comprises a plurality of paddles 55 which extend radially outwardly from the screw 146 adjacent the shaft 142, the paddles 55 interspersed with flights 147, and preferably disposed in approximately 90° increments around the shaft 142.

The paddles 55 may have heads 56 which may be parallel to the direction of conveyance 145, or may be disposed at an angle with respect thereto from 0 to 90°, to assist in the conveying action and/or to provide a different action on the pulp during tumbling. In the FIGURE 6 embodiment, the ozone containing gas is introduced at a multiplicity of points at connection 57, along the bottom, and ultimately gas to be discharged will flow out vent 130. Ozone-containing gas can also be added to the pulp at the reactor inlet. In this embodiment it will be seen that in addition to flowing cross-current to the direction of pulp conveyance 145, the gas also flows counter-current.

In the FIGURE 7 embodiment, the reactor 59 includes both a screw 46 and a screw 146 therein, with the shafts 42, 142 rotated by motors 43, 143 which move counter-current to each other. The reactor shell 60 is large enough to accommodate both of the counter-rotating screws. The counter rotation of the screws results in effective mixing action as the pulp moves from pulp inlet 61 at the top of the shell 60 to the pulp outlet 62 at the bottom of the shell 60 and at the opposite end thereof. Although not shown in the FIGURE 7 embodiment, the same type of ozone gas introducing structures as shown in the FIGURES 3 or 6 embodiment are utilized.

In the FIGURE 7 embodiment, the reactor 59 --instead of having two different types of screws 46, 146 -- may have two screws 46, or two screws 146.

FIGURE 8 illustrates yet another embodiment reactor according to the invention. The FIGURE 8 embodiment structure that is comparable to those in the FIGURE 3 embodiment are shown by the same reference numeral only preceded by a "2".

In this embodiment, the means for conveyance of the pulp comprises only a very short screw section 246, having between one and two complete flights 247 disposed just below the pulp inlet 222. The means for effecting tumbling comprise the paddles 64 which are disposed on the shaft sleeve 65 surrounding the shaft 242 and keyed thereto, or otherwise rotatable therewith. The paddles 64 may have the pulp engaging faces 66 thereof an angle of 0 to 90° to the direction of pulp conveyance 245, and depending upon the particular angle thereof with respect to the direction of rotation of the shaft 242, the paddles 64 may assist somewhat in pulp conveyance too.

In the preferred embodiment illustrated in FIGURES 8 and 9, the paddles 64 are disposed at every approximately 90° around the shaft sleeve 65, and define the outline of a helix (one or more helices).

It has been found according to the invention that the tangential velocity of the tips 67 of the

paddles 64 is a key to getting optimum tumbling action, so that the pulp remains loose and the maximum amount of surface area thereof is exposed to the ozone containing gas within the shell 241. It has been found that if the distal ends 67 of the paddles 64 have a tangential velocity such that the pulp will follow a ballistic arc around the top of the vessel, so that the pulp will have optimum looseness and optimum surface area exposed to the ozone containing gas.

In the FIGURES 10 and 11 embodiment, a reactor 70 is illustrated which has a significantly different way in which it affects tumbling action than the reactors heretofore desired. In the FIGURE 10 embodiment, the reactor 70 is shown basically in association with other components in the general type of apparatus as illustrated in the FIGURE 2 embodiment, including in association with a cyclone separator 36.

The reactor 70 includes a tubular shell 71, having packing areas 72, 73 for sealing purposes. The shell 71 is rotatable about an axis 74 concentric therewith. It is rotated about the axis 74 by two or more rollers 75 which engage the bottom of the outer periphery of the shell 71, one or more of the rollers 75 being rotated by the motor 76. In this embodiment, the conveyance means comprises means for mounting the shell 71 so that the axis 74 thereof tilts downwardly an angle  $\beta$  from the pulp inlet 77 to the pulp outlet 78. The angle  $\beta$  is chosen so that it is sufficient to effect uniform movement of the high consistency pulp within the reactor 70 at a speed desired -- e.g. the angle  $\beta$  in the exemplary embodiment illustrated in the drawings being about  $5^\circ$  to  $15^\circ$ . The tumbling action is provided by the rotation of the shell 71 itself about the axis 74. While structures within the shell 71 attached to the inner circumferential periphery 79 are not necessary in order effect the tumbling action, lifters, bars, or other structures may be provided if desired.

Optimum tumbling action occurs utilizing the reactor 70 when the shell 71 is rotated about the axis 74 at a rotational speed sufficient to effect movement of the pulp from a bottom portion of the shell to the top of the shell so that it falls down from the top of the shell to the bottom, but the speed must be insufficient to cause the pulp to follow along with the shell top during rotation (that is by centrifugal action essentially attach itself to the shell 71).

The pulp outlet 78 of the reactor 70 must include means for lifting the pulp effectively to the level of the axis 74 to be discharged thereat. In the embodiment actually illustrated, the discharge structure at outlet 78 includes a semi-circular trough 80 which has a discharge screw 81 therein rotatable with shaft 82 powered by motor 83.

Curved lifting plates 84 extending generally radially inwardly from the inner peripheral surface 79 of the shell 71 engage any pulp beneath the trough 80, and effect lifting of it above the screw 81, to be dumped into the trough 80 and conveyed in the direction of pulp conveyance 85 out of the shell 71 by the screw 81. From the screw 81 the pulp leads to a fan 87, from there to a cyclone separator 88 which separates and recycles ozone containing gas 89, while the pulp flows into standpipe 39 and is ultimately pumped therefrom by low or medium consistency pump 40 at the bottom thereof.

While the system of FIGURES 10 and 11 may be operated with sufficient ozone containing gas in the pulp actually being conveyed into the reactor 70 by the pneumatic conveyance system, under some circumstances it will be desirable to add ozone to the reactor 70. This may be provided by disposing a pipe 91 at the inlet 71 so that it is concentric with the axis 74 and is stationarily mounted to the bottom discharge 92 from the cyclone 36. The hollow pipe 91 is attached to the ozone source 19, and has a plurality of openings (not shown) disposed along the length thereof. As shown FIGURES 10 a number of headers 99 can be used to recycle the ozone containing gas, similar in principle to FIGURE 9, and additional feed of ozone may be provided by line 98. If lifters are provided extending inwardly from the inner circumferential peripheral surface 79 of the reactor 70 at the position of the pipe 91, they will terminate short of the pipe 91.

It is to be understood that each of the embodiments of reactors illustrated in FIGURES 3, 6, 7, 8 and 10 may be utilized as the ozone reactor in the apparatus of either the FIGURES 1 or 2 embodiments. Also, the pulp conveyance mechanism may be a combination of a screw and incline of the reactor shell, rather than one or the other. Also, in situations where paddles or lifters are provided, the paddles or lifters within the reactor may be disposed at different angles and/or have different radial extents in order to optimize tumbling action. Also, in each case the ozone gas flow within the reactor may be co-current, counter-current, cross-current, or a combination thereof. The FIGURES 8 and 10 embodiments may be superior in a number of situations since they have less mechanical structures to interfere with the mass transfer within the reactor, although all of the embodiments can effectively delignify pulp with ozone.

It should be understood that all of the reactors according to the invention will be operated at much less than full capacity of the reactor vessel (e.g. shell 41). It is desirable that no more than about one-half of the interior volume of the reactor vessel is filled with pulp in order for the tumbling action according to the present invention to effectively

take place, optimizing mass transfer. In typical situations, the amount of ozone by weight in the carrier gas is about 6%, and the amount of ozone by weight applied to the pulp is about one-half percent.

An exemplary method of delignifying pulp utilizing the apparatus heretofore described will now be set forth with specific reference to the FIGURES 1 and 8 embodiment.

Comminuted cellulosic fibrous material is thickened to high consistency at press 15, and sufficient acid is added from source 13 so that its pH is within the range of about 1.5-4.0. The thickened pulp is shredded at 17 and fluffed at 18, the fluffing causing the pulp to be loose with a high surface area to volume ratio. Ozone containing gas -- typically with an oxygen carrier gas and about 4-8% by weight of ozone within the carrier gas, and about one-half percent by weight on the bone-dry pulp -- is added at the fluffer 18, and by a conduit 24, 224 to the bottom of the reactor 23, 223. Sufficient ozone is in the gas to be effective to delignify the pulp.

The pulp is maintained in contact with ozone containing gas for at least a few seconds while it is tumbled to keep the fluffed pulp loose and homogenous, with a high surface area to volume ratio, well mixed with the ozone containing gas. This is accomplished by rotating shaft 242 so that the distal ends 67 of the paddles 64 have a tangential velocity sufficient to impart a ballistic velocity to the pulp, as the pulp is conveyed by screw section 246 in direction 245 from the pulp inlet 222 to the pulp outlet 225. The volume of gas necessary to effect delignification is minimized by continuously withdrawing and reintroducing the gas into the reactor 223 utilizing fans 226 and reintroduction nozzles 227, so that the gas vented in vent 230 has a greatly reduced ozone content compared to the gas introduced in the inlet 224.

During treatment, the pulp typically has a consistency of over 20%, and preferably about 30-40%, and while its retention time may vary from a few seconds upward to several minutes depending upon ozone concentration, size of the reactor, consistency of the pulp, etc., typically the pulp is maintained in the reactor 223 about one-three minutes. While temperature and pressure are not critical, the preferred temperature range is about 20-50°C, and the preferred pressure is from slightly sub-atmospheric to about 15 psi.

It will thus be seen that according to the present invention a method and apparatus have been provided for effectively bleaching paper pulp with ozone gas. While the invention has been herein shown and described in what is presently conceived to be the most practical and preferred embodiment thereof, it will be apparent to those of

ordinary skill in the art that many modifications could be made thereof within the scope of the invention, which scope is to be accorded the broadest interpretation of the appended claims so as to encompass all equivalent processes and structures.

## Claims

1. A method of delignifying acidified comminuted cellulosic fibrous material at high consistency, comprising the steps of: (a) fluffing the material (with 18) so that it is loose, with a high surface area to volume ratio; and (b) adding ozone containing gas (at 22, 24) to the material, the amount of ozone added being effective to delignify the material; and characterized by the step of  
(c) maintaining the material in contact with ozone containing gas for at least a few seconds, while tumbling the material (with 47, 48, 64, etc.) to keep the fluffed material loose and homogenous, with a high surface area to volume ratio, well mixed with the ozone containing gas.
2. A method as recited in claim 1 further characterized in that step (c) is practiced by simultaneously tumbling the material and continuously conveying it in a first direction (45, 245).
3. A method as recited in claim 1 further characterized in that the material has a consistency of about 25-45% through treatment.
4. A method as recited in claim 2 characterized by the further step (e), during the practice of step (c), of, at a plurality of places along the path of the material as it moves in the first direction, continuously introducing (at 27, 227) and withdrawing (at 26, 226) ozone containing gas from contact with the material.
5. A method as recited in claim 4 further characterized step (e) is practiced by introducing at some places (27, 227) along the path gas withdrawn from a previous place (26, 226) along the path.
6. A method as recited in claim 1 utilizing a reactor comprising a central shaft (242) having a plurality of paddles (64) extending radially outwardly therefrom to facilitate the tumbling action of the material, each paddle having a distal end (67) remote from the shaft; and further characterized in that step (c) is practiced by rotating the paddles with the shaft (by

243) about a generally horizontal axis of rotation so that the tangential velocity of the paddle distal ends is sufficient to impart a ballistic velocity to the pulp such that the arc described by the particles follows the arc of the vessel shell.

7. A method as recited in claim 3 further characterized in that step (c) is practiced so that the retention time is about 1-3 minutes, and wherein the material has a pH of about 1.5-4.0, and at a temperature of about 20-50° C, and at a pressure from slightly below atmospheric to about 15 psi.
8. Apparatus for delignifying paper pulp using ozone containing gas, comprising: (a) means (18) for fluffing paper pulp so that it is loose and has a high surface area to volume ratio; (b) an ozone reactor (23, 223) comprising a tubular shell elongated in a first generally horizontal dimension; (c) a pulp inlet (22, 222) to said tubular shell adjacent a first end thereof in said dimension of elongation, and a pulp outlet (25, 225) therefrom adjacent a second end thereof, opposite said first end; and (d) means for conveying the pulp from the inlet to the outlet; and characterized by
- (e) means for effecting tumbling of the pulp as it moves in the reactor from the inlet to the outlet so that the pulp remains loose with a high surface to volume ratio, comprising a plurality of paddles (64) extending radially outwardly from a shaft (242) and spaced from each other along said first dimension; and characterized in that said means (d) comprises a short screw section (247) on said shaft (242) between said inlet and said paddles.
9. Apparatus as recited in claim 8 further characterized by: (f) means (224, 227) for introducing ozone containing gas into said shell at a plurality of locations along said first dimension, the gas flowing generally perpendicular to said first dimension, and means (226) for withdrawing ozone containing gas at locations located above each means for introducing gas, the withdrawal locations (226) being connected to subsequent introduction locations (227) along the first dimension.
10. Apparatus for delignifying paper pulp using ozone containing gas, comprising:
- (a) means (18) for fluffing paper pulp so that it is loose and has a high surface area to volume ratio;
- (b) an ozone reactor comprising a tubular shell (71) elongated in a first generally hori-

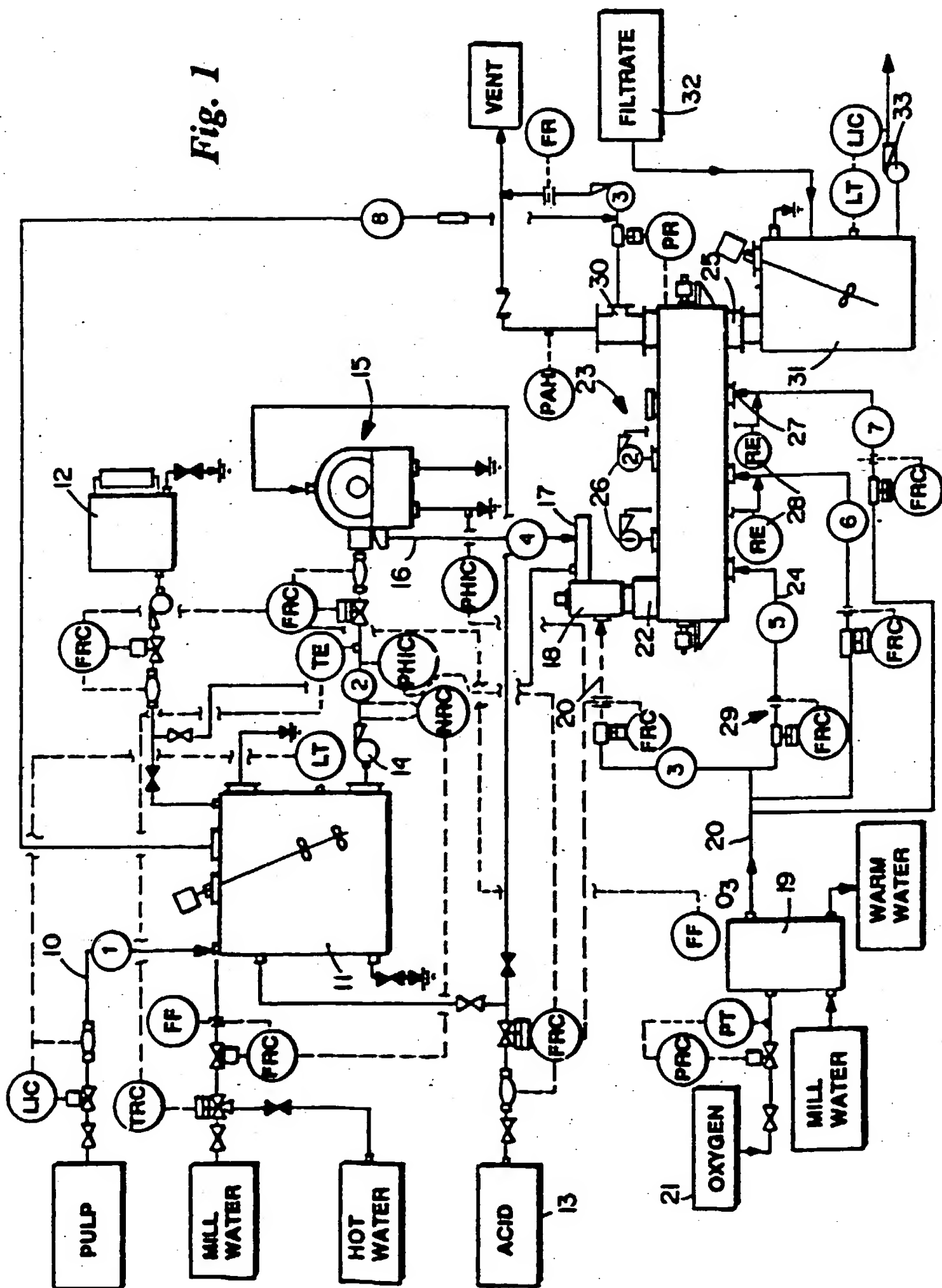
zontal dimension;

(c) a pulp inlet (77) to said tubular shell adjacent a first end thereof in said dimension of elongation, and a pulp outlet (78) therefrom adjacent a second end thereof, opposite said first end;

(d) means for conveying the pulp from the inlet to the outlet, including means (75) for mounting said shell so that said first dimension slants downwardly from said pulp inlet end toward said pulp outlet end; and

(e) means for effecting tumbling of the pulp as it moves in the reactor from the inlet to the outlet so that the pulp remains loose with a high surface to volume ratio, comprising means (76) for rotating said shell about a central axis extending in said first dimension.





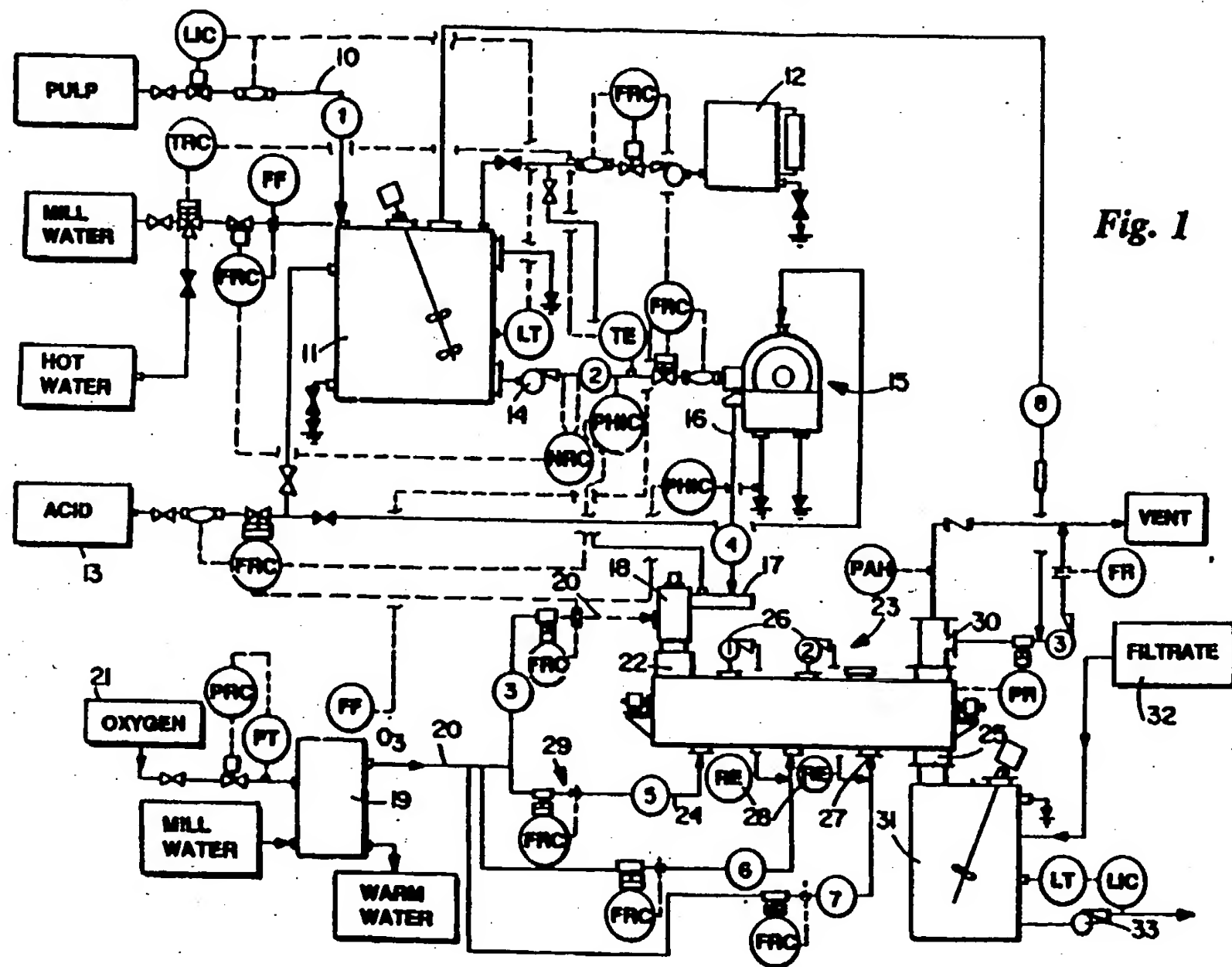


Fig. 1

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Fig. 2

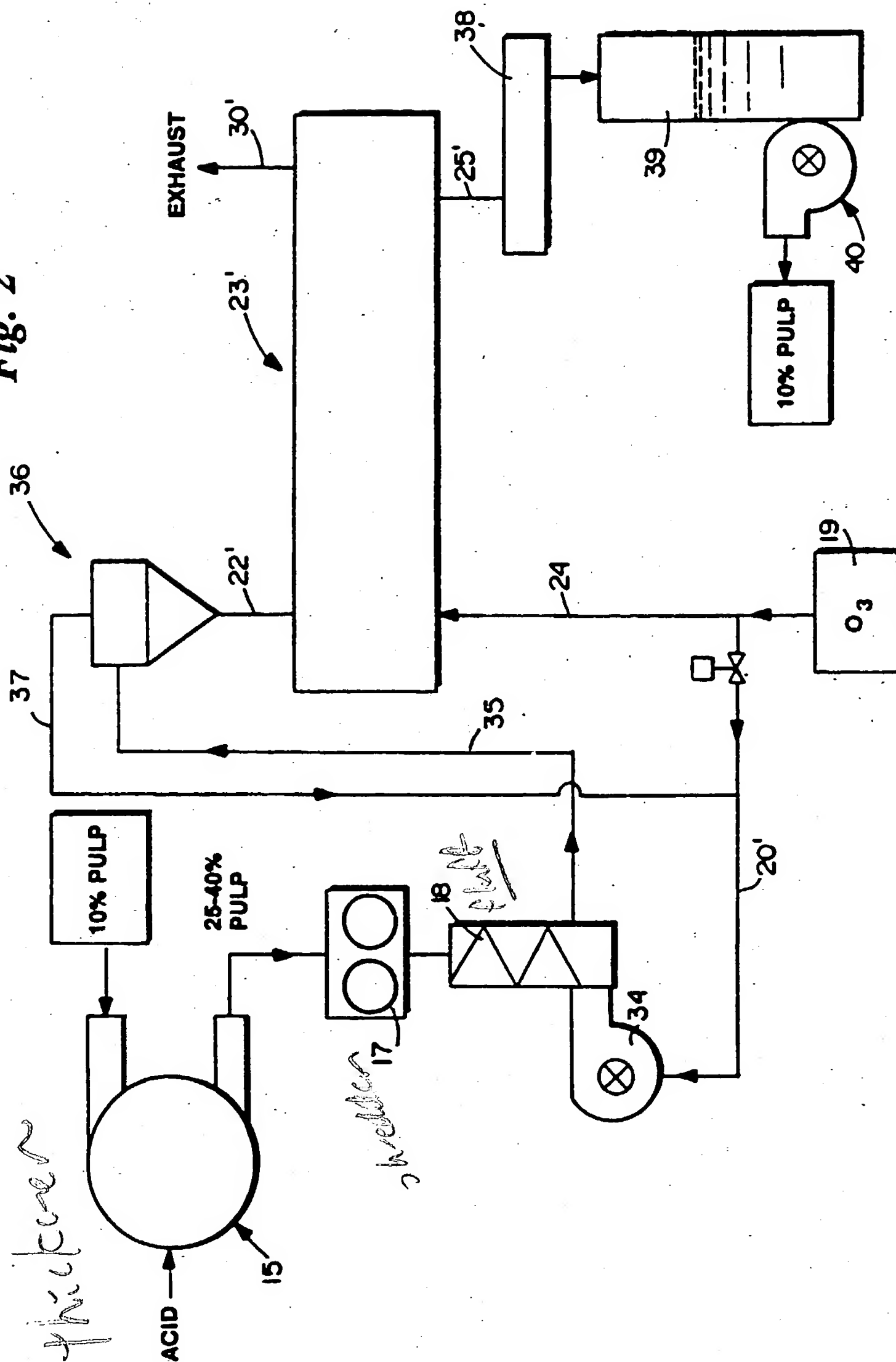


Fig. 3

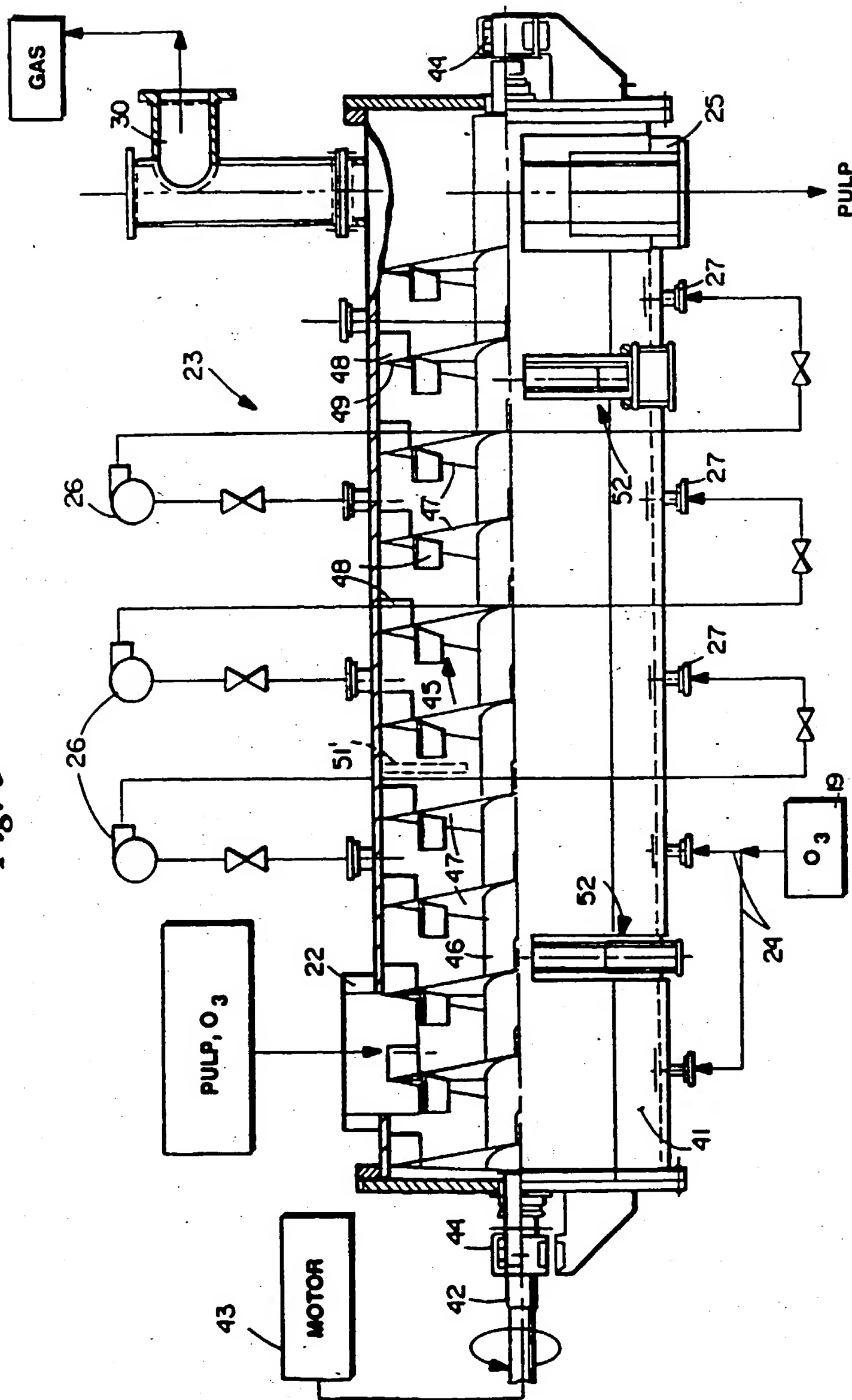




Fig. 4

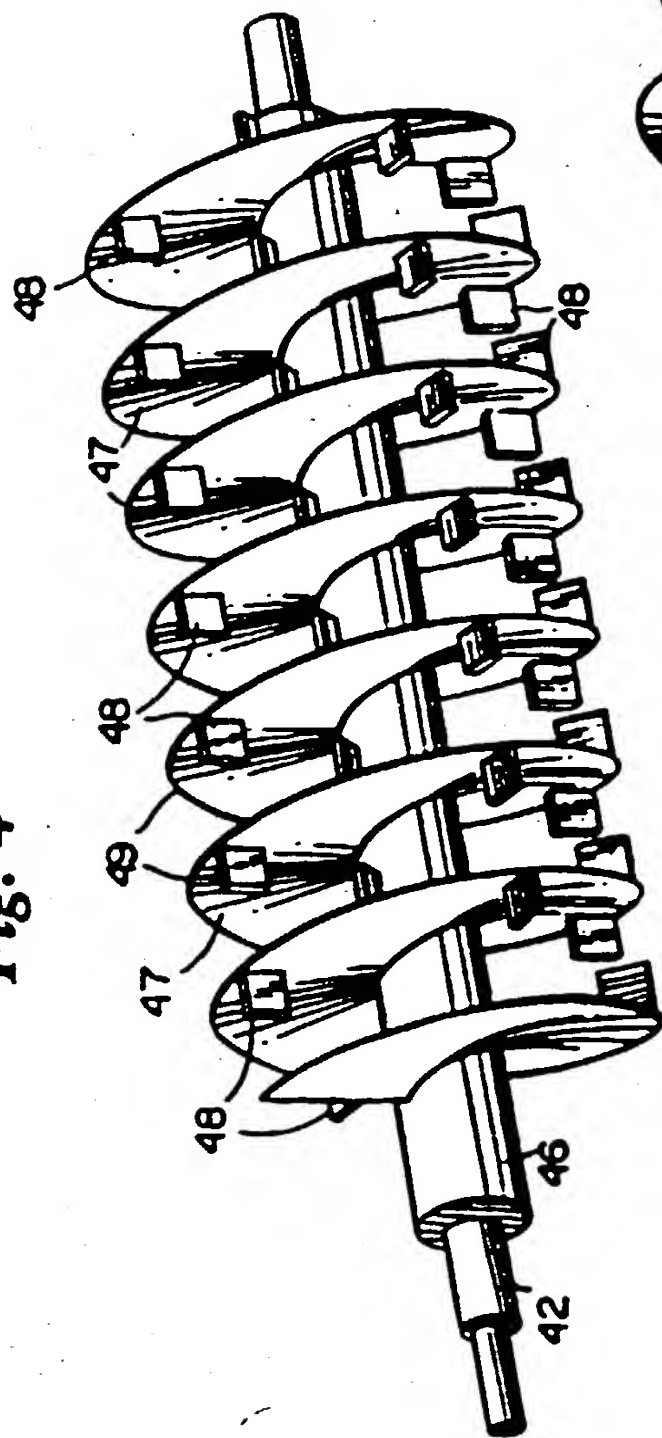


Fig. 5

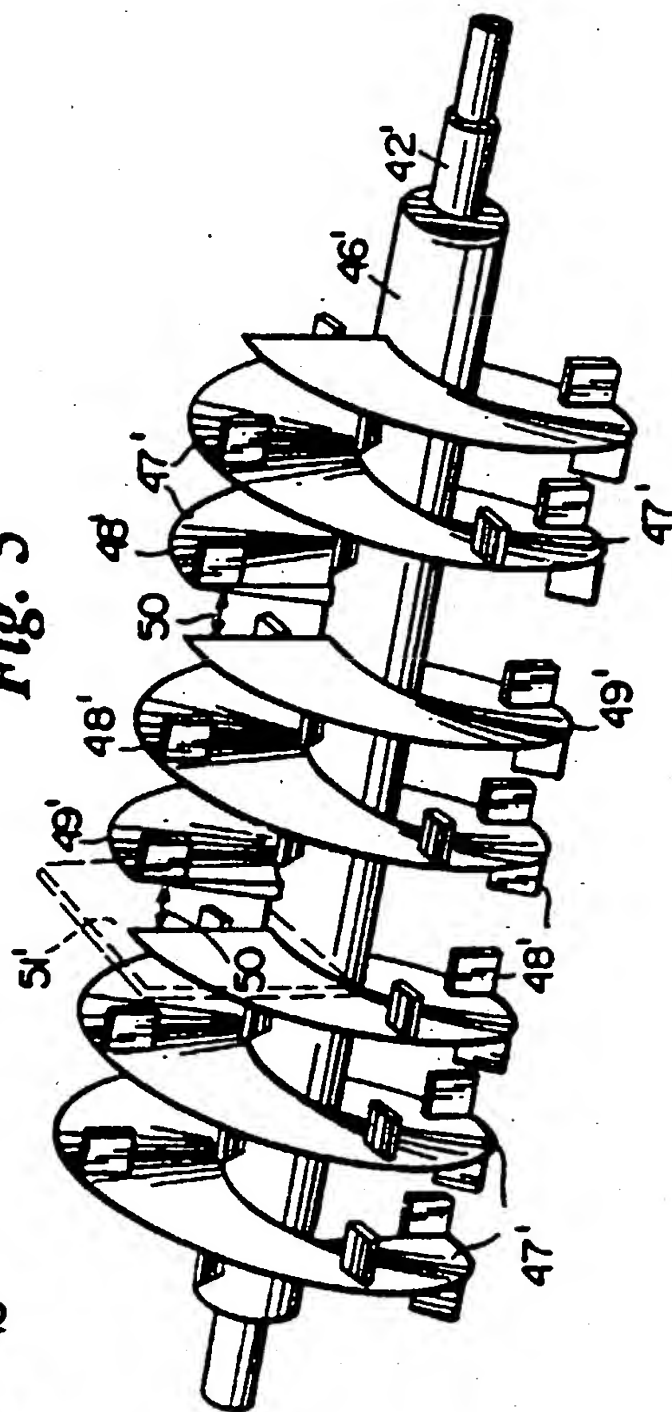


Fig. 6

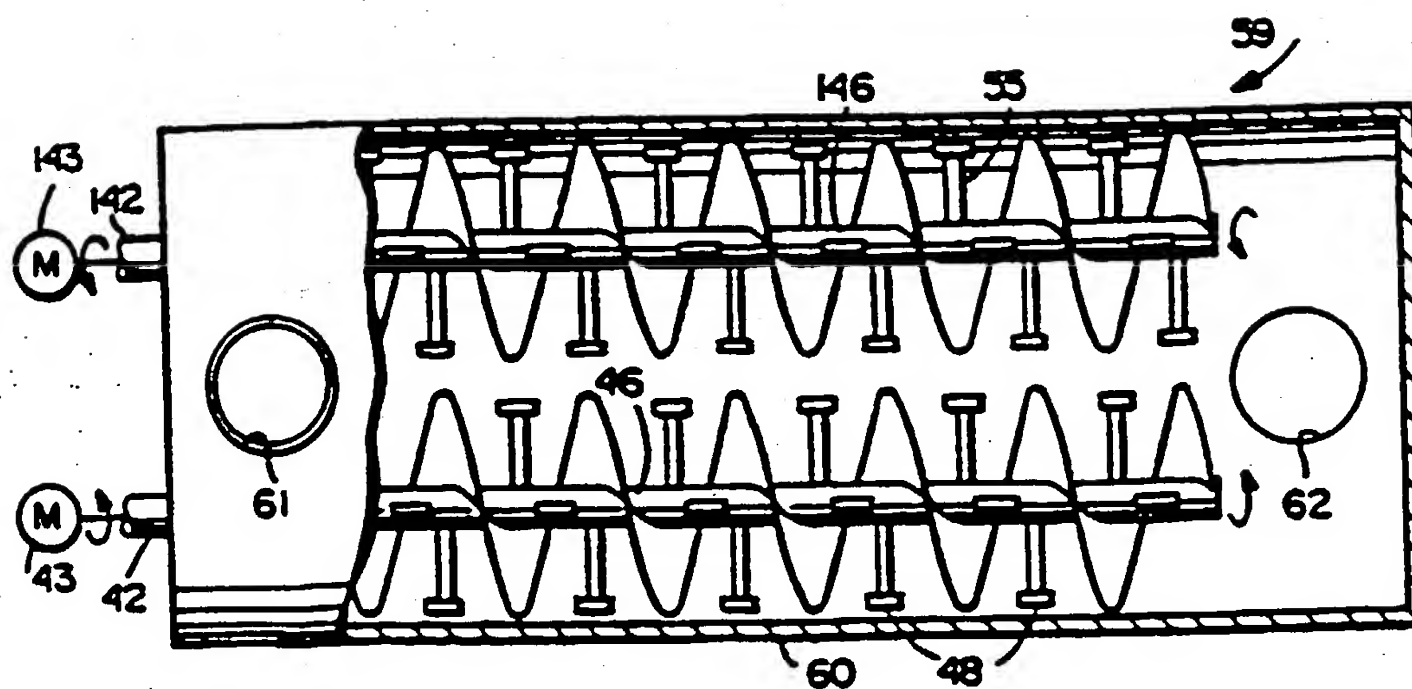
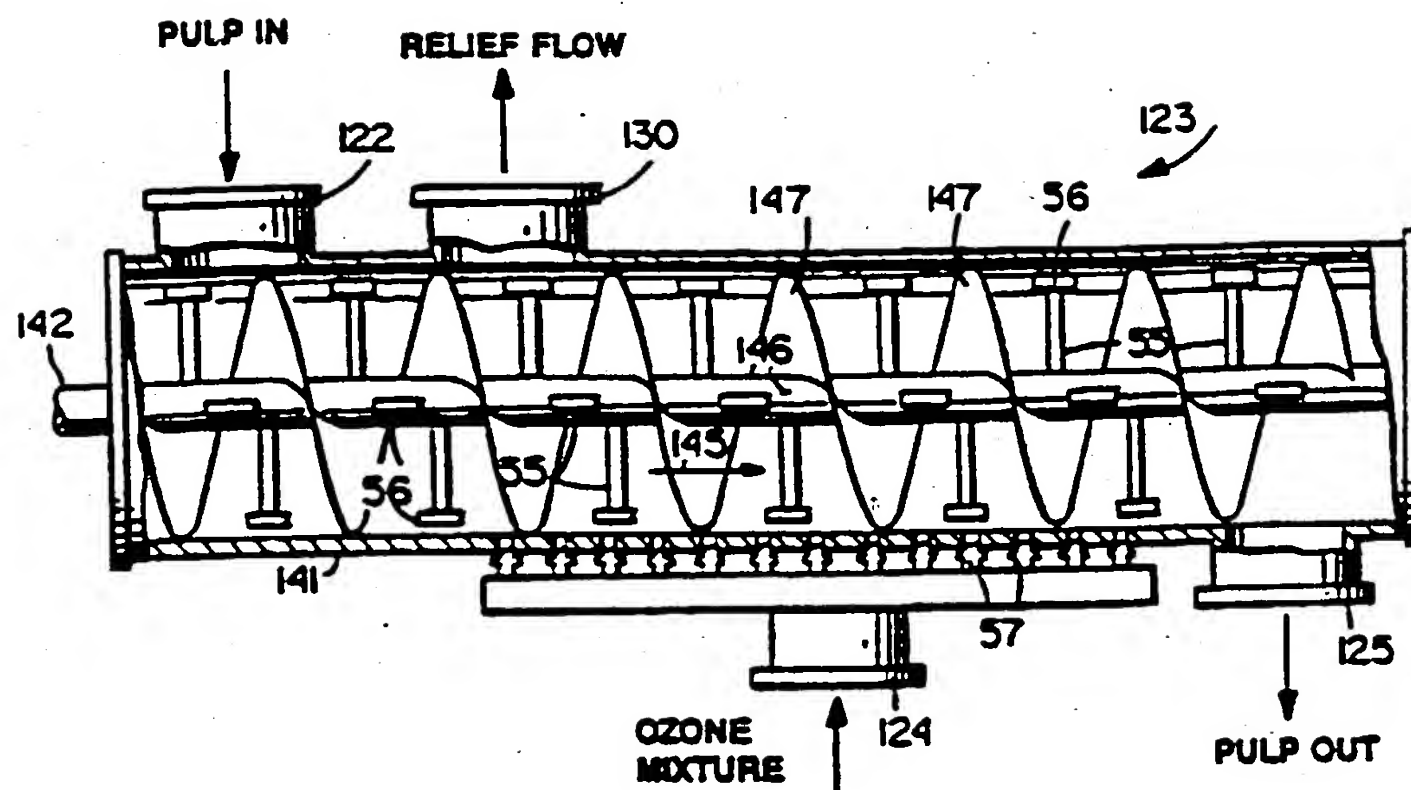
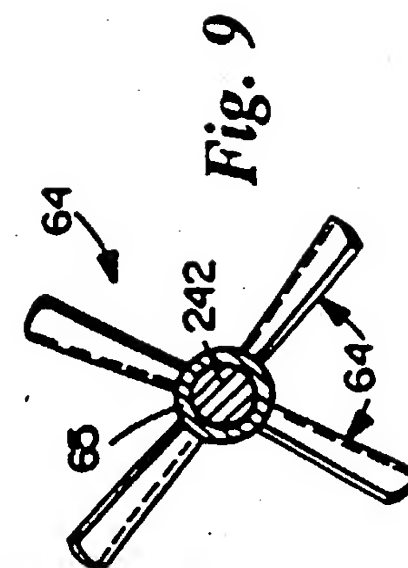
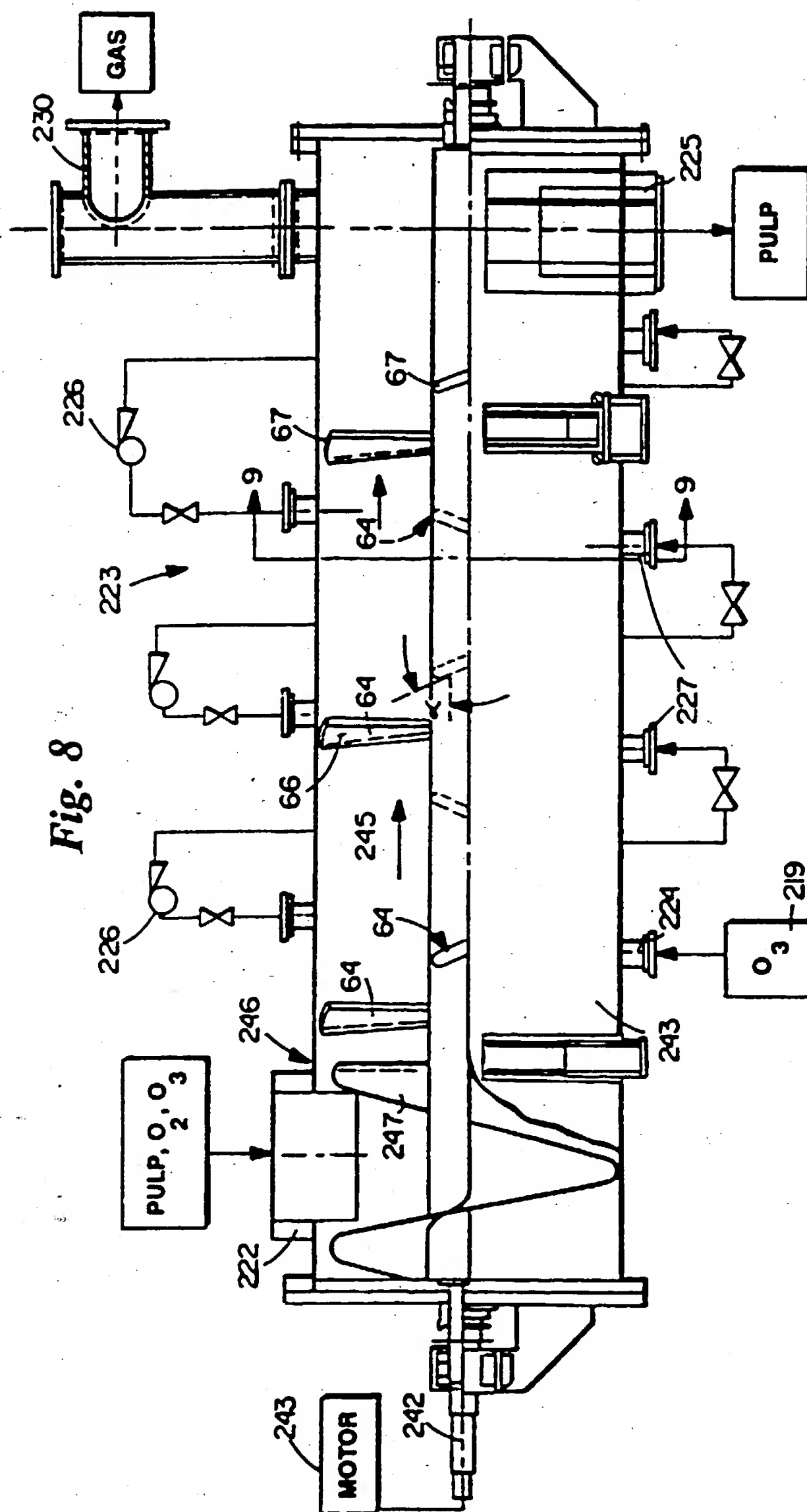


Fig. 7



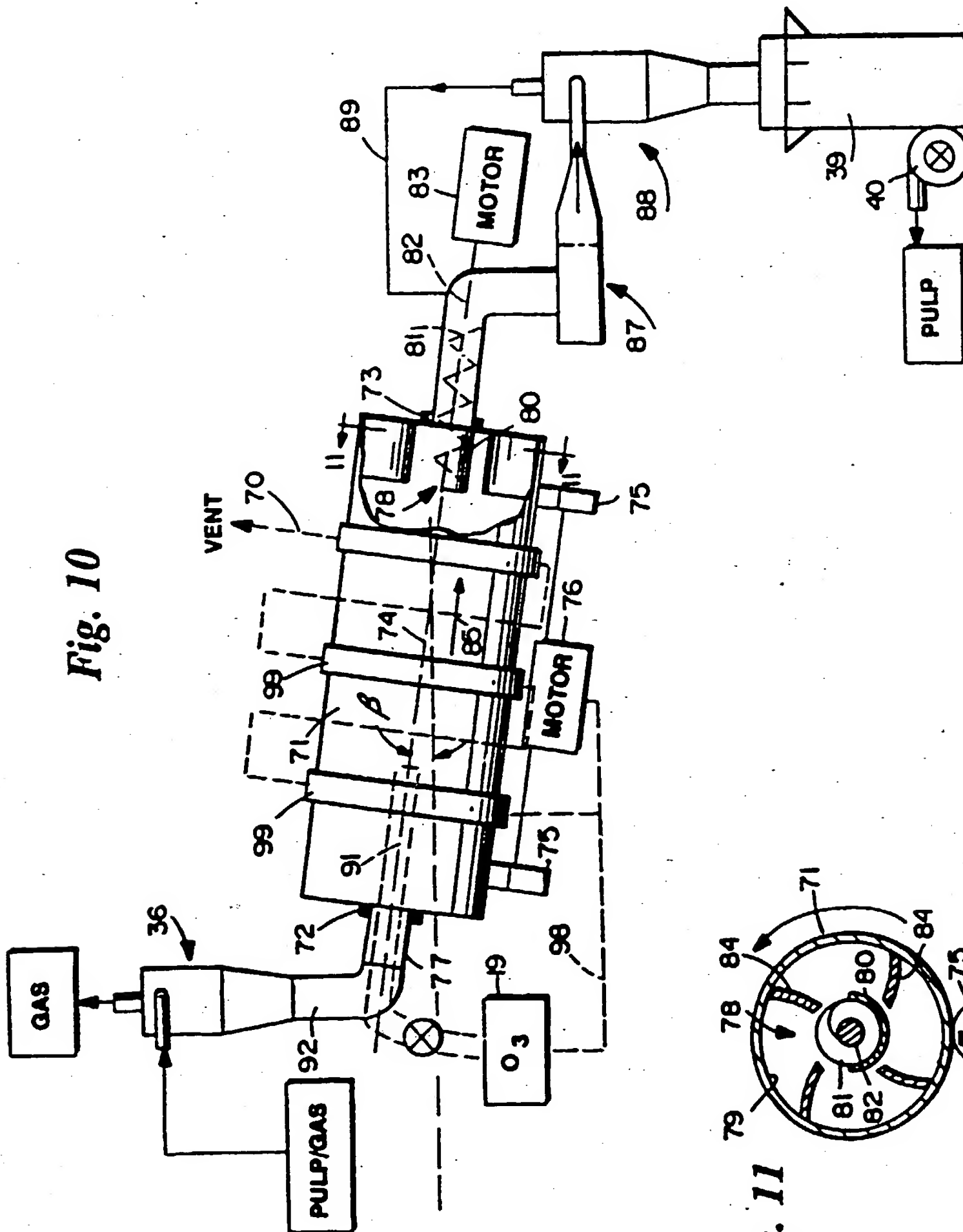


Fig. 10

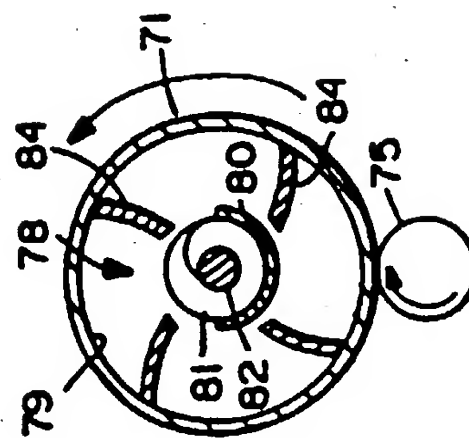


Fig. 11